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Progress made on three research projects during an eighteen month period is described. In the first project, reactions of halogen amines with excess H or D atoms were studied as sources of excited NF and NCl. The reaction of H/D with nitrogen trichloride was scaled to reagent and product densities about 100 times greater than those of previous experiments. The density of excited NCl produced by this system was observed to scale linearly with the reagent densities. The second project probed energy transfer between NCl and iodine atoms. Excited iodine was produced efficiently from NCl generated in the scaled up nitrogen trichloride reactor. In the final project, the intrinsic rates of radiative and collisional relaxation of excited NCl were investigated.

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INTRODUCTION

This report describes progress made on the research program "Reactions and Spectroscopy of Excited Nitrenes" during the eighteen month period between 1 July, 1990 and 31 December, 1991. Because of a lapse in funding for the program, work was stopped at the end of this period and hence this document represents a final report of the work done. Funding for the program was resumed on 1 May, 1992 and the research is again proceeding well.

The broad objectives of the program include defining new means for the generation of halogen nitrene metastables, measuring the properties of processes by which these metastables transfer the energy they carry to laser candidate species, and probing the kinetics and mechanisms of second order reactions and energy transfer processes which may occur in the systems under high density conditions. Considerable progress toward these objectives was made during the period described by this report. Research was performed on three distinct projects, which investigated the reactions of halogen amines (sources of halogen nitrene metastables), the excitation of iodine atoms by energy transfer from excited NCl, and the rates of radiative and collisional decay of excited NCl. The data obtained served to indicate the good potential that these systems have for lasing in the visible and near IR regions of the spectrum, and defined the directions for continuing research now underway in our laboratory.
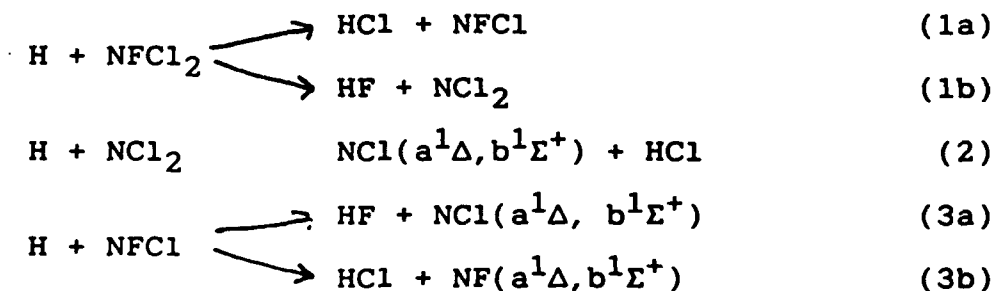
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SUMMARY OF RESULTS

## Reactions of Energetic Halogen Amines

The first project undertaken as part of this program was an investigation of the reaction of $NFCl_2$ with H atoms. This work was performed with additional support from a second AFOSR supported grant (AFOSR - 90 - 0259, "Physical Chemistry of Energetic Nitrogen Compounds"). The experiments made use of a small discharge - flow reactor in which gaseous $NFCl_2$, a stable compound synthesized and purified in our laboratory,[1] was allowed to react with excess hydrogen or deuterium atoms. The atoms were created by a microwave discharge through H_2 or D_2 flows diluted in Ar, or by creation of H_2 or D_2 with fluorine atoms which were generated by a discharge through CF_4 diluted in Ar. The objective was the simultaneous production of both $NF(a^1\Delta)$ and $NCl(a^1\Delta)$ by the following sequence of reactions:

$$H + NFCl_2 \longrightarrow HCl + NFCl \qquad (1a)$$
$$ \longrightarrow HF + NCl_2 \qquad (1b)$$

$$H + NCl_2 \qquad NCl(a^1\Delta, b^1\Sigma^+) + HCl \qquad (2)$$

$$H + NFCl \longrightarrow HF + NCl(a^1\Delta, b^1\Sigma^+) \qquad (3a)$$
$$ \longrightarrow HCl + NF(a^1\Delta, b^1\Sigma^+) \qquad (3b)$$

The reaction does indeed produce chemiluminescence from both the $a^1\Delta$ and $b^1\Sigma^+$ states of both NF and NCl. The $a^1\Delta$ states are the preferred products, and our data indicated that the overall mechanism generated about a ten-fold excess of NF(a) over NCl(a), as determined from absolute intensities of the emissions from these molecules. Hence, paths 1a and 3a above predominate. From the

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time profile of the NCl b --> X emission over a range of H atoms densities, the rate constant of the rate limiting step was determined to be $2.5 \pm 0.2 \times 10^{-12}$ $cm^3 s^{-1}$. By comparison with rate constants[2,3] for the analogous H atom reactions with NF_3 and NF_2 (H + NF_3 being very much slower than H + F_2), it was originally thought that this rate constant applied to process 1a/1b.

Although these experiments were performed at very low reagent densities ($NFCl_2$ at roughly 10^{12} cm^{-3}), evidence of second order energy pooling between NF(a) and NCl(a) was readily observed. In this process energy transfer between these two species occurs to generate NF(b) and NCl(X):

$$NCl\ (a^1\Delta) + NF(a^1\Delta) \longrightarrow NF(b^1\Sigma^+) + NCl(X^3\Sigma^-) \qquad (4)$$
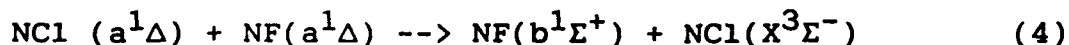
For experiments in which the H atoms were replaced by D atoms (in order to avoid NF(a) + HF(v) energy pooling),[4] the NF(a), NCl(a), and NCl(b) signals scaled linearly with the $NFCl_2$ density, whereas the NF(b) signal scaled as the $NFCl_2$ density raised to the 1.6 power. This behavior is shown in Figure 1. Benard[5] has reported that process (4) can be catalyzed by the admission of iodine atoms to the system. In this case, NCl(a) efficiently excites the iodine atoms to the $^2P_{1/2}$ state, and the excited iodine then excites NF(a) to the NF(b) state. This process is described in more detail below. The iodine catalysis was readily accomplished in our experiments by the admission of small flows of HI, which reacted with the F atoms and H atoms in the flow (H atoms were made by the F + H_2 reaction) to generate I atoms. For admission of an HI flow about 20% of the F atom flow, the NCl(a)
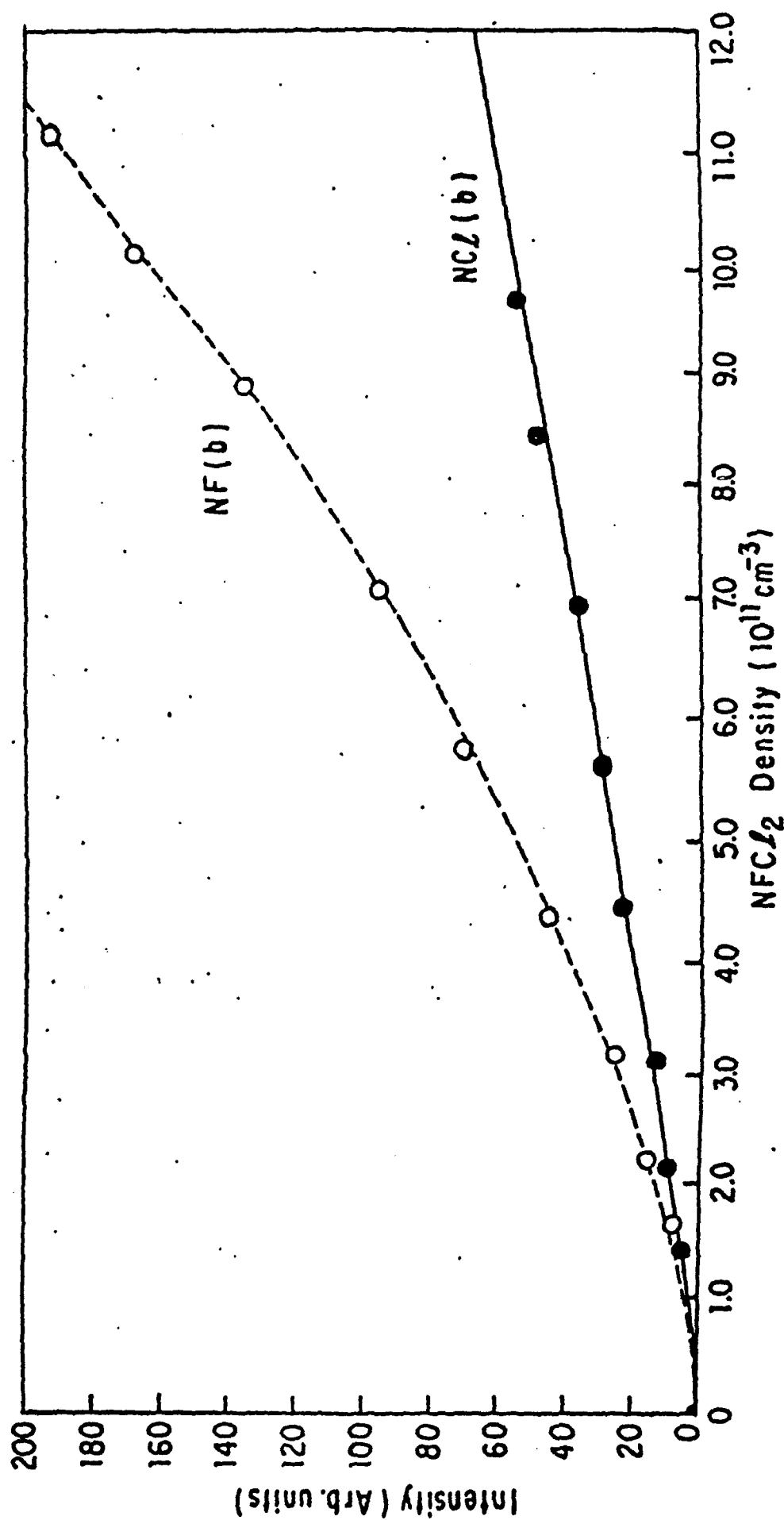
Figure 1. Intensity of emission from NF(b) and NCl(b) vs. the initial density of $NFCl_2$. The lines through the data are least squares fits. NCl(b) is linear with the $NFCl_2$ density, whereas NF(b) varies as $[NFCl_2]^{1.6}$

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signal was completely quenched, the NF(a) signal was reduced by 15%, and the NF(b) signal increased by a factor of four. This behavior is shown in Figure 2. Clearly, these energy pooling mechanisms are rapid and efficient processes which can occur readily in this system.

The results of this project were published as an article[6] in the Journal of Physical Chemistry in 1991, and a number of other groups became interested in the chemistry. In particular, Professor D.W. Setser of Kansas State University has set up an $NFCl_2$ generator in his laboratory and made measurements of the H + $NFCl_2$ reaction by observing emission from the vibrationally excited HF and HCl produced in the mechanism. Setser's measurements, which isolate reaction (1), suggest[7] that 1a dominates over 1b, and that the rate constant for 1a is on the order of 10^{-11} cm^3s^{-1}. If this is indeed the case, then our rate constant must apply to reaction 3a/3b. Setser also finds a somewhat larger proportion of NCl(a) produced in reaction 3. In large measure, these data substantiate our original findings and lend further support for the utility of an $NFCl_2$ system in a potential SWCl device base on the NCl(a)/NF(a) medium. Apart from the simultaneous generation of the NF and NCl metastables, $NFCl_2$ appears to be a stable, · rable reagent which might be used as a high pressure gas, a ma; : advantage for any practical device.

A second part of this project involved an initial scale - up of the H + NCl_3 mechanism, a halogen amine system which produces a high yield of NCl(a). This reaction was originally studied[8] in our laboratory in 1990, and is thought to proceed by a two step mechanism analogous to that discussed above:
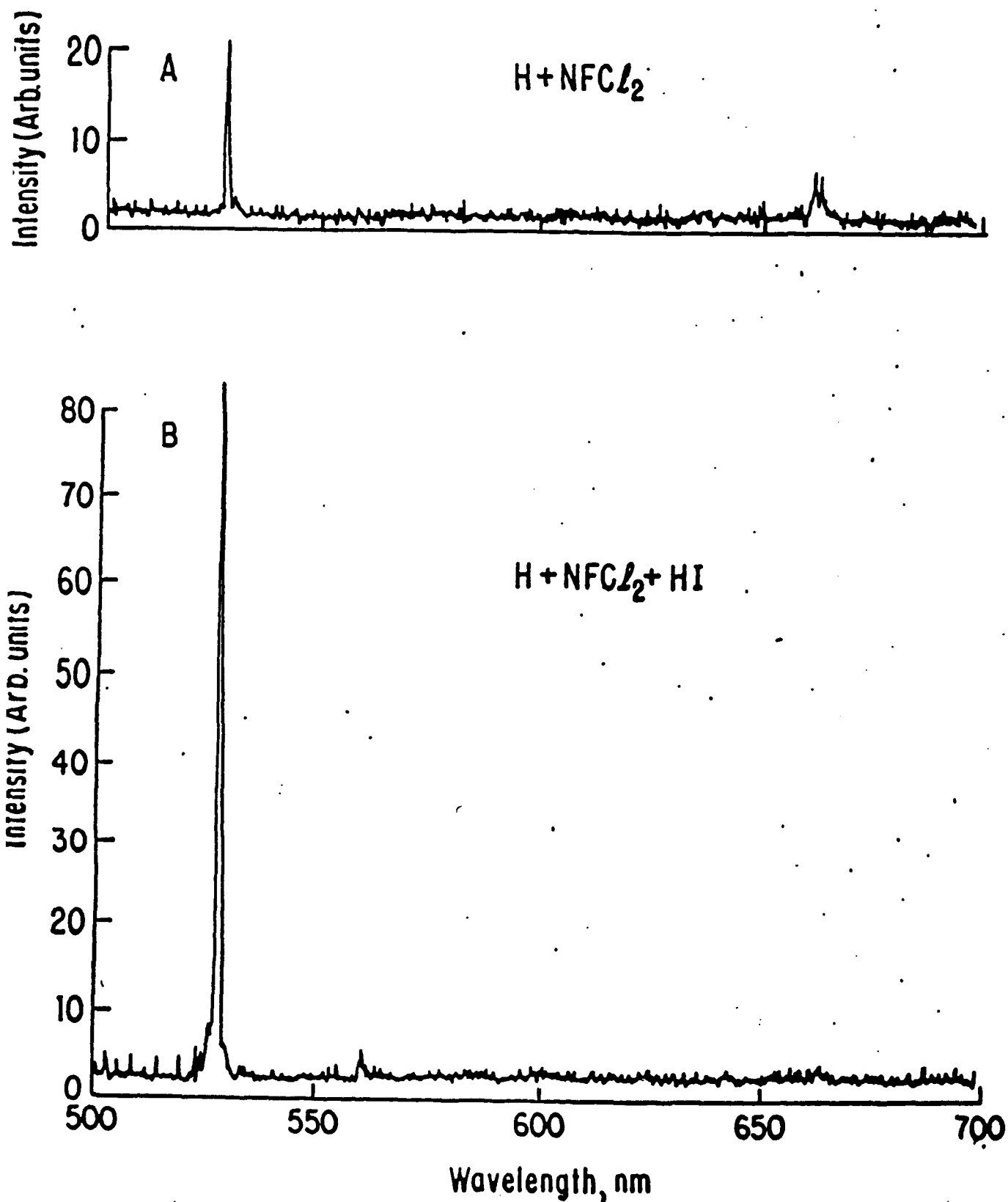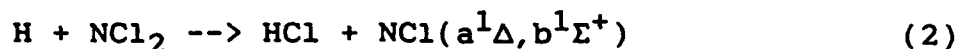
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Figure 2. Emission spectra from H + NFCl$_2$ without and with HI added. The intensity scales in A and B are the same.

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$$H + NCl_3 \longrightarrow HCl + NCl_2 \tag{5}$$

$$H + NCl_2 \longrightarrow HCl + NCl(a^1\Delta, b^1\Sigma^+) \tag{2}$$

A rate constant $k = 4.0 \times 10^{-12}$ cm^3s^{-1} was determined for the rate limiting step, which we now believe to be 2b. The rate constant for the fast step (2a) is close to 10^{-10} cm^3s^{-1}, although this value is certain to within only a factor of two. In process 2b, NCl is formed in the $a^1\Delta$ state preferentially over the $b^1\Sigma^+$ state by a very large ratio, and the absolute branching fraction to the $a^1\Delta$ state has a lower limit of 0.2. The actual branching fraction to NCl(a) is thought to be much greater than this value, since the analogous $H + NF_2$ reaction produces NF(a) with a branching fraction[9] of 0.91.

Our initial experiments on the $H + NCl_3$ reaction were performed with a small discharge flow reactor like that used for the $NFCl_2$ investigation described above. The objectives of the initial scale - up were to increase the reagent densities by about two orders of magnitude, to ascertain whether the density of the NCl(a) product scaled linearly with this increase, and to investigate any deleterious second order processes which might become evident. For example, there is one report in the literature[5] which suggests that the rate constant for NCl(a) self removal (i.e., the NCl(a) + NCl(a) --> products reaction) is very large at 8×10^{-12} cm^3s^{-1}. This rate would severely limit any NCl(a) - based laser system, and should be evident for NCl(a) densities as low as 10^{13} cm^{-3}.

The scaling experiments made use of a transverse flow reactor which is diagrammed in Figure 3. The reactor was fabricated
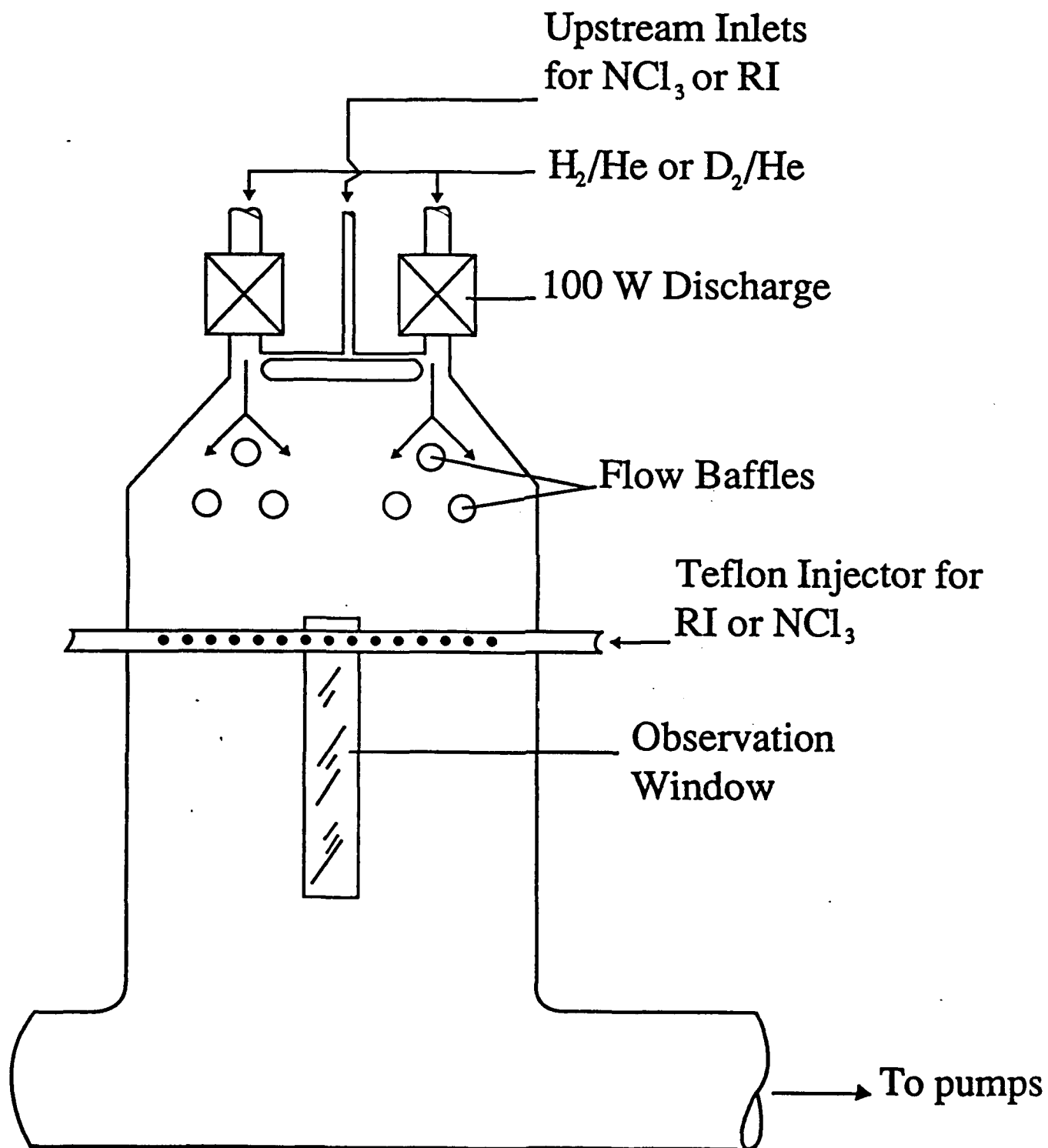
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Figure 3. Transverse flow reactor

from aluminum and had a 30 cm long flow region with a 1 cm x 25 cm cross section. The inside surfaces of the reactor were coated with halocarbon wax to reduce wall losses of reactive species. The reactor was pumped by a 1000 l/min mechanical pump, generating a linear flow velocity of 650 cm/s at the operating pressure of the experiments. H or D atoms were produced by passage of H_2/He or D_2/He through two 100W microwave discharges in parallel with one another. Titrations of the H atom flows in the reactor indicated that atoms densities up to 10^{15} cm^{-3} could be generated with this apparatus. NCl_3 was generated by using methods previously developed in our laboratory,[10] i.e., bubbling a Cl_2/He mixture through an acidified saturated solution of $(NH_4)_2SO_4$. The NCl_3 was swept from the solution by the He flow and trapped at 193K. The pure NCl_3 was allowed to warm to room temperature and was subsequently entrained in He for use in the H + NCl_3 experiments. The NCl_3/He flow was admitted to the reactor via a perforated teflon injector as shown in Figure 3. The proportion of NCl_3 in the NCl_3/He flow admitted to the reactor was determined by UV absorption at 254 nm. These measurements indicated that NCl_3 densities of greater than 10^{14} cm^{-3} could be obtained in the flow reactor.

Chemiluminescence produced in the reactor was observed through a 2.5 X 15 cm quartz window positioned just downstream of the teflon injector as shown in Figure 3. The emission was chopped at 313 Hz and collected by a fiber optic bundle, which transmitted the light to the entrance slit of a 0.275 m monochromator. The dispersed emission was detected by either a cooled intrinsic Ge detector or by a cooled GaAs photomultiplier

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tube. The response of either detector was amplified by a lock -
in amplifier and recorded with a strip chart recorder. The re-
sponse of the entire detection system was calibrated vs. wave-
length with a standard tungsten - halogen lamp.

The spectra of visible and near IR emissions generated by
admission of NCl_3/He to the H or D atom flows were identical to
those observed in previous low density experiments, with substan-
tially increased signal to noise ratios resulting from higher
densities of the emitters. No features attributable to states
other than NCl(a) or NCl(b) were observed. In particular, no N_2
first positive emission was seen, in keeping with the low density
results. The absence of N_2 emission indicates that second order
side reactions analogous to those found[11] in the H + NF_2 system
do not occur even for the higher reagent densities of the present
experiments.

Admission of NCl_3 to the H atom stream produced an intense
red flame (corresponding to the NCl b --> X emission) which ex-
tended for several ms downstream of the mixing zone. The dura-
tion of the flame corresponded well with the limiting rate of
formation of excited NCl characterized by the rate constant noted
above (4 x 10^{-12} cm^3s^{-1}). Similar time behavior was measured for
the NCl a --> X emission measured with the Ge detector, with the
exception that the entire time profile was somewhat extended
relative to the b --> X time profile, corresponding to the longer
lifetime of NCl(a) in the system. From the risetime of the
a --> X emission (just longer than the mixing time), this life-
time was still considerably shorter than the time constant for

NCl(a) formation, correspondidng to the decay of the emission downstream. Clearly, the NCl(a) was rapidly quenched by collisions with the reactor walls or the molecules of the reagent stream.

Figure 4 shows a plot of the relative NCl a --> X emission intensity vs. the initial density of NCl_3 in the flow. For the data shown, the NCl_3/He mixture was admitted through the upstream inlets rather than the teflon injector. It is clear that the NCl(a) density scales linearly with the NCl_3 flow, up to the maximum flows achievable with our apparatus. The scatter in the plot corresponds in large measure to the uncertainty in the absolute densities of the NCl_3. The observed linear scaling corresponds to the linear increase in the rate of production of NCl(a) with increasing NCl_3 flow, opposed by a relatively constant (and greater) rate of decay as above. The scaling indicates that the NCl(a) decay rate does not increase with NCl_3 flow, suggesting that deleterious second order processes are not significant at the densities of our experiments.

It would appear that the NCl(a) density in the system is limited by quenching at the walls or by collisions with the H/H_2 stream. Since no N_2 first positive emission is observed, quenching by H atoms (as in the H + NF_2 system)[11] is unlikely. Further, the H_2 is present in very high densities (approaching 10^{17} cm^{-3}), such that it could have a major effect even for inefficient quenching. H_2 can quench NCl(a) by an E to V process as follows:

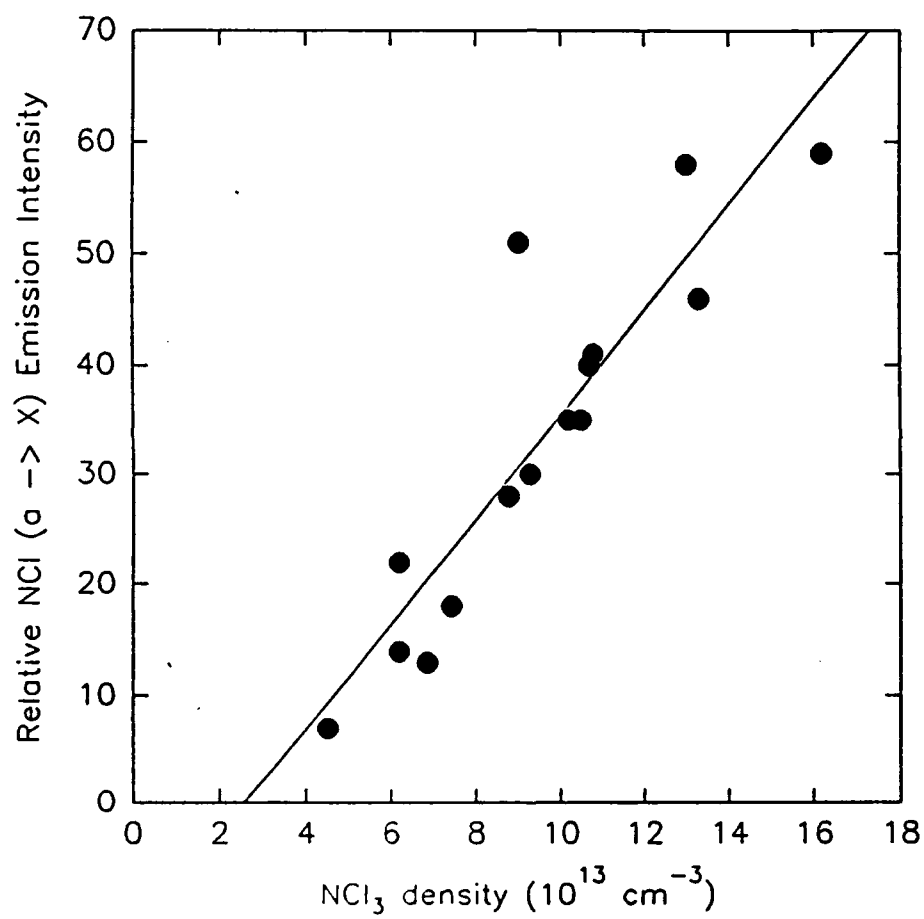$$NCl(a,v=0) + H_2(v=0) \longrightarrow NCl(X,v=0) + H_2(v=2) + 1200 \ cm^{-1} \qquad (6)$$
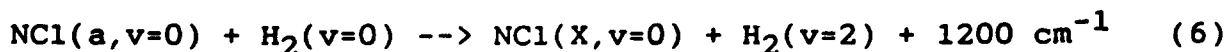
Figure 4. Scaling plot for the production of NCl ($a^1\Delta$) by the H + NCl$_3$ system.

To test this hypothesis, the H_2 flow was replaced by D_2. For identical flow conditions, the NCl a --> X intensity was five times greater for NCl_3 reaction with D/D_2 than with H/H_2.

The absolute densities of NCl(a) produced in the reactor were determined by calibrating the intensity of the NCl a --> X emission with chemiluminescence from a standard, in this case the O + NO reaction. This method has been used a number of times previously in our laboratory, and has been described in detail elsewhere.[12] The density of NCl(a) is given by:

$$[NCl(a)] = \left(\frac{S_{NCl}}{S_{NO_2}}\right)\left(\frac{k_{1.08}[O][NO]}{A_{NCl}}\right) \tag{7}$$

where S_{NCl} and S_{NO_2} are the intensities of the recorded emissions, A_{NCl} is the radiative rate of the NCl a --> X transition (taken to be 0.7 s^{-1}),[13] $k_{1.08}$ is the rate constant for production of NO_2 photons[14] at 1080 nm by the O + NO reaction ($k_{1.08} = 3.67 \times 10^{-21}$ $cm3$ $molecule^{-1}$ s^{-1} $\overset{.}{A}^{-1}$), and [O] and [NO] are densities determined by measured flow rates and titration. From this calibration, the NCl(a) density produced in the reactor was 1.0×10^{13} cm^{-3} for maximum flows of D_2 and NCl_3. The uncertainty in this determination is on the order of 50%, largely because of uncertainties in the calibration procedure and in the value of the NCl a --> X radiative rate. Nonetheless, it is clear that the NCl(a) density is indeed substantial, corresponding to about 10% of the initial NCl_3 density. We note again that the NCl(a) density is limited largely by quenching in the system (probably by collisions with D_2, present in very high density)

rather than by the dynamics of its formation chemistry or by deleterious second order effects.

Excitation of Iodine Atoms by NCl(a)

In 1991, Bower and Yang[15] reported their observation of the excitation of iodine atoms by energy transfer from NCl(a):

$$NCl(a^1\Delta) + I^2P_{3/2} \longrightarrow NCl(X^3\Sigma^-) + I(^2P_{1/2}) \qquad (8)$$
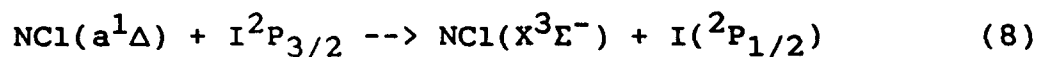
Their data (taken under steady state conditions in a flow reactor) suggested that the overall quenching of NCl(a) by iodine atoms is fast ($>10^{-10}$ cm^{3}s^{-1}) and efficiently produces excited I $^2P_{1/2}$ (hereafter I*). The occurrence of the energy transfer was subsequently verified by Benard and co-workers[5] and by work in our laboratory.[6] From this preliminary work, NCl(a) would appear to offer an interesting alternative to $O_2(a^1\Delta)$ for pumping iodine atoms, and perhaps a number of other halogen or pseudo-halogen species.

The specific objective of this project was to ascertain whether the H + NCl$_3$ system for the generation of NCl(a) can be effectively used for the production of I*. The initial experiments were performed usin; the low density discharge flow apparatus employed in our ori;. .. work with the H + NCl$_3$ and H + NFCl$_2$ reactions. In these ··; ::ents, NCl(a) was generated by the admission of gaseous NC: ; ·) a stream containing an excess density of H atoms. Its pre··nce was monitored via the a --> X emission in the near IR at 1.077 μm. Iodine atoms were produced in the stream by the admission of HI, as in the experiments with NFCl$_2$ described above. The admission of HI to the flow produced

an intense I $^2P_{1/2}$ --> I $^2P_{3/2}$ chemiluminescence signal at 1.315 μm (as viewed through a 0.25 m momochromator by an intrinsic Ge detector cooled to 77K). Removal of the NCl_3 flow quenched the I* emission by more than 95%, indicating that only a very small fraction of the emission was attributable to the well studied[16] H + HI reaction and subsequent H_2 - I energy transfer process. This relationship was quantified by monitoring the decay of the NCl(a) chemiluminescence vs. the growth of the I* chemilumines- cence as the flow of HI was increased, and these data are shown in Figure 5. Clearly, the I* in the system is produced from NCl(a). Calibration of the response of the detection system (monochromator and detector) and comparison of the NCl(a) inten- sity with the I* intensity indicated that the absolute intensity of the I* emission was many times greater than the absolute in- tensity of the NCl(a) emission that was quenched. This is as expected, since the radiative rate for the I* --> I transition is about an order of magnitude greater than that for the NCl a --> X transition, and because energy transfer to iodine atoms is likely to be a much more probable event than NCl a --> X radiation. Here again, the observation of these processes at such low densi- ties ($<10^{12}$ cm^{-3}) for NCl a and I) testifies to their speed and efficiency.

Based on these very positive preliminary results, the pro- duction of I* by energy transfer from NCl(a) was also tested in the higher density regime by using the transverse flow reactor described above. In this apparatus, iodine was admitted to the flow as HI or I_2 (the latter entrained in He) via the perforated
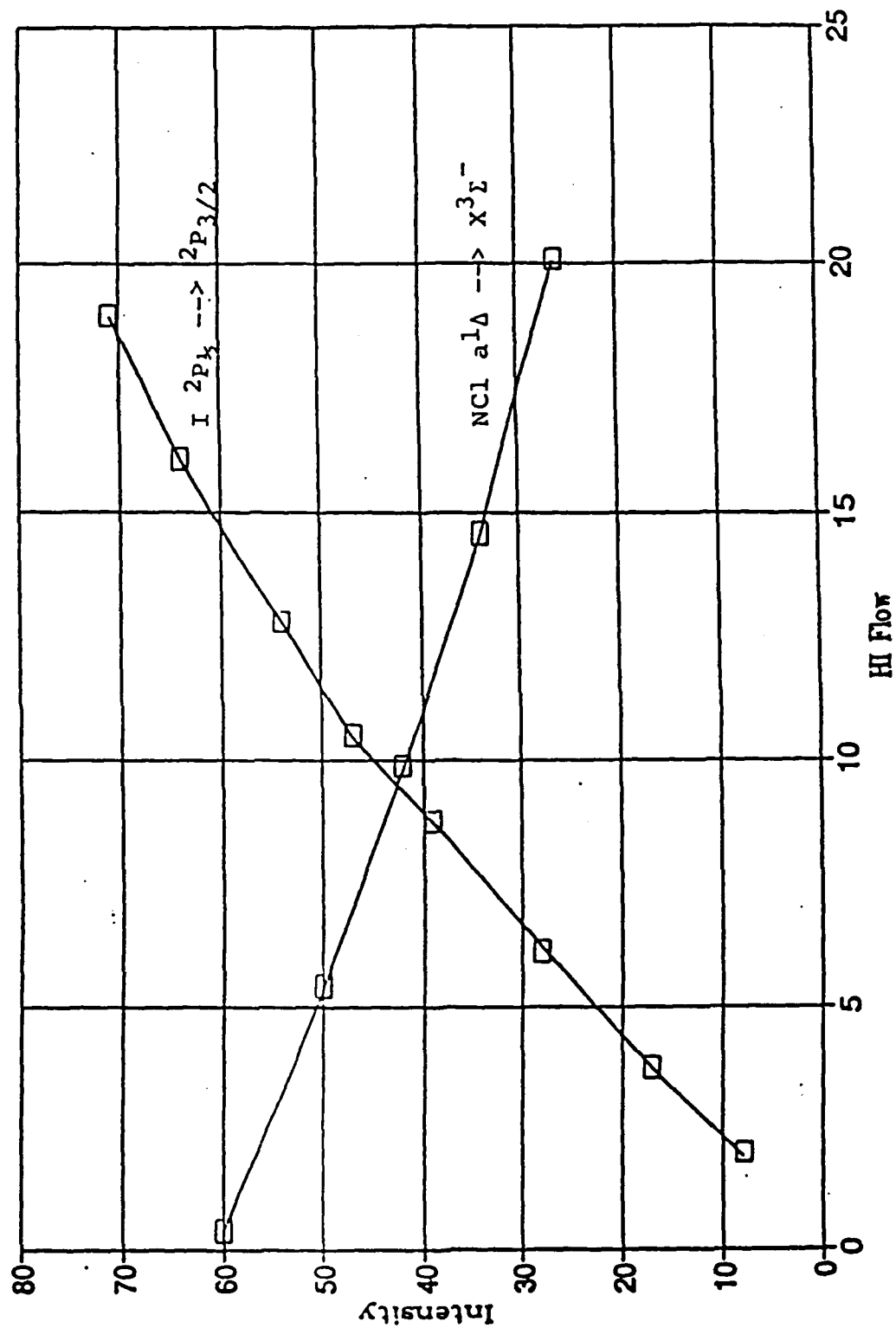
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Figure 5. Rise of I* chemiluminescence and decay of NCl(a) chemiluminescence as a function of the HI flow.

teflon injector or through inlets positioned just downstream of the discharges. Intense I^* emission at 1.315 μm was readily generated in both cases. Increasing flows of HI or I_2 quenched the 1.077 μm emission from NCl(a), and produced the 1.315 μm emission in a symmetrical manner (much like the data in Figure 5 above). Since the H + HI reaction gives rise to a background I^* signal as described above, experiments with HI were limited to lower HI flows where the I^* emission produced from NCl(a) clearly dominated over the background. In this regime, the intensity of the I^* signal produced by the admission of HI to the NCl(a) flow was 10 to 20 times greater than that of the initial NCl(a) signal. Ratios of this magnitude were not achieved when I_2 was used as a reagent, although much larger flows could be admitted without background interference. For the maximum H and NCl_3 flows, the optimum flow of I_2/He gave rise to an I^* signal 5 times more intense than the initial NCl(a) signal. The time profile of this signal exhibited a short rise and a decay over more than 10 ms. The decay was longer than that of the NCl(a) signal, corresponding to a convolution of the NCl(a) formation rate and the lifetime of I^* in the system.

The absolute density of I^* present in the flow was determined from the relative intensities of the NCl(a) and I^* emissions, with an absolute calibration of the wavelength response of the light collection and detection system. The relative densities of I^* and NCl(a) are given by:

$$\frac{[I^*]}{[NCl(a)]} = \left(\frac{S_I}{S_{NCl}}\right)\left(\frac{A_{NCl}}{A_I}\right)\left(\frac{\gamma_{1.3}}{\gamma_{1.08}}\right) \qquad (9)$$

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where S_I and S_{NCl} are the measured intensities, A_I and A_{NCl} are spontaneous emission rates, and $\gamma_{1.3}$ and $\gamma_{1.08}$ are response factors for the detection system. For an NCl(a) density of 2×10^{12} cm^{-3}, obtained using H atoms as a reagent, the I* density was found to be a nearly equivalent value. Presumably the densities of both species could be increased to near 10^{13} cm^{-3} by using D atoms as a reagent, as per the discussion above.

Clearly, NCl(a) is efficiently converted to I* in this system. In principle, the I* density could be much greater than the initial NCl(a) density, since the NCl(a) density is limited by quenching in collisions with H_2 or D_2. If enough iodine were present to dominate the NCl(a) quenching, virtually all of the excited NCl generated by the D + NCl_3 system could be converted to I*. This was not possible in the present experiments because of the very large density of D_2 present in the flow. The system does not appear to be limited by the dynamics of the formation of NCl(a) or by the dynamics of the energy transfer to iodine, but simply by the generation of a large flow of D atoms in an environment which does not include high densities of quenchers. The present results, in which I* densities about an order of magnitude less than that realistically required for lasing were generated in spite of a very inhospitable reagent stream, bode well for continued progress toward a new I* laser.

Radiative and Collisional Relaxation of Excited NCl

A third project we have worked on during this reporting period has involved measurement of rate constants for spontaneous

emission and collisional quenching of NCl(a). The NCl a --> X
radiation rate has been an issue for a number of years, and is
thought[5,13] to have a value on the order of 1 s^{-1}. After exten-
sive experiments and a number of modifications to our apparatus,
we have made significant progress toward measurement of this
important parameter. The configuration of the experiment is
shown in Figure 6. Chlorine azide (ClN_3) and diluent are passed
at small flow rates through a large photolysis cell fabricated
from 10 cm i.d. pyrex drain pipe. The ends of the cell are
sealed with quartz windows for transmission of the photolysis
beam, from a pulsed KrF laser at 249 nm. Radiation at this wave-
length is known[17] to dissociate ClN_3 to NCl(a) + N_2. The excimer
laser is positioned more than 10 m away from the cell, such that
divergence of the beam produces a laser spot sufficient to fill
the window as the beam enters the cell. The photolysis beam is
reflected back through the cell by an overcoated aluminum mirror
positioned behind the rear window. This diffuse irradiation is
such as to make net diffusion of the excited NCl(a) photoproduct
out of the cone of sight of the detector (a Ge detector which
views the emission through a narrow band filter at 90°C to the
photolysis beam) very s! ↲. For typical experimental conditions
(about 3 Torr of the Cl⌣ ⌣ nix), calulated diffusion times were
on the order of 500 ms. ⌣ ⌣, since the emission fills the cone
of sight of the detector ⌣⌣ht collection is efficient and only
very small densities of the parent ClN_3 are needed to produce an
emission signal with an adequate signal to noise ratio. Hence,
NCl(a) quenching by collisions with the parent azide or by col-
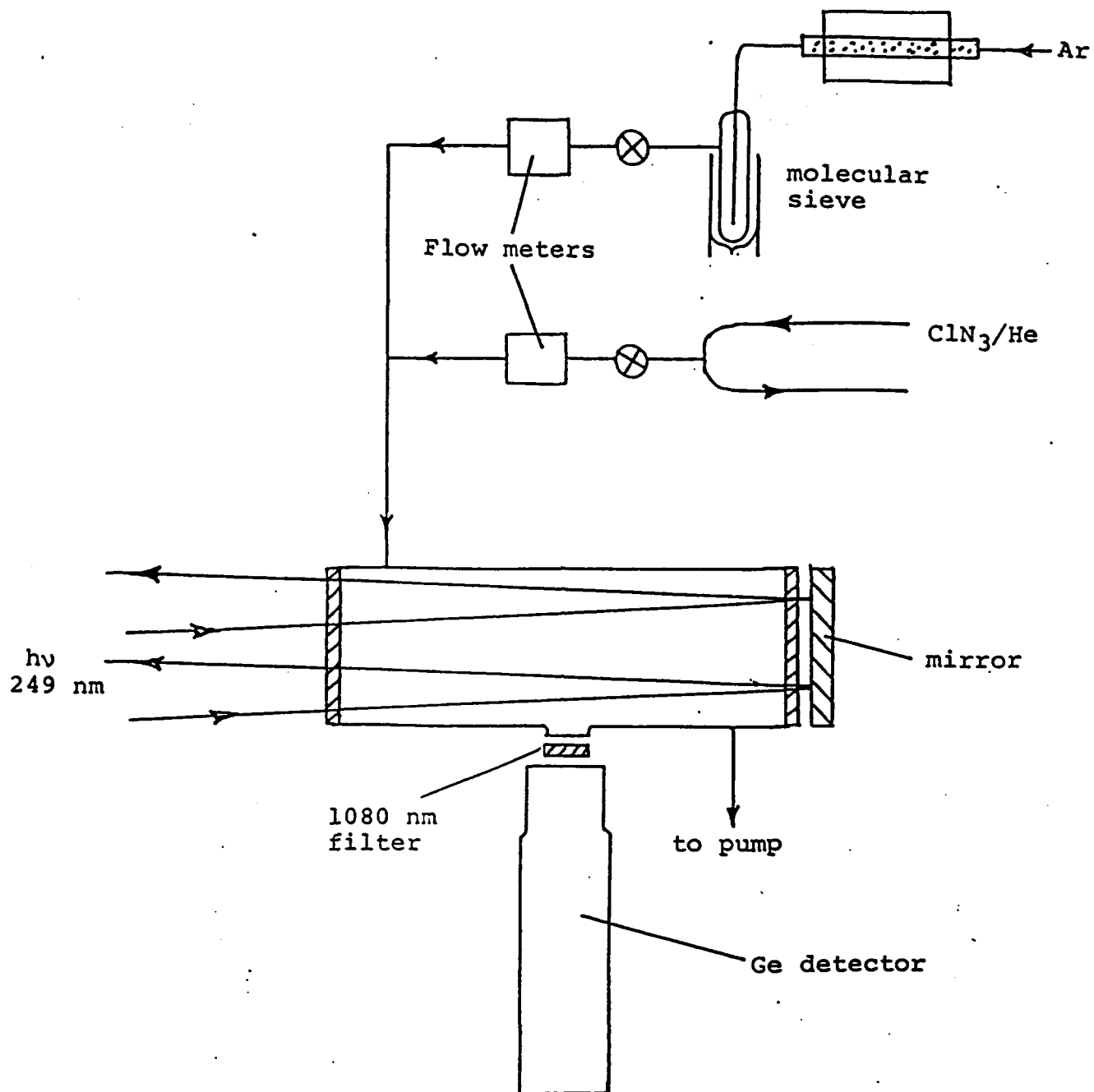lisions with other NCl(a) molecules (reported to be an efficient

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Figure 6. Apparatus used for measurement of NCl a --> X time decays

process) is also very slow. Since total pressures of several Torr are required to slow diffusion rates in the system, purity of the diluent is a key factor. Although we have found that ultra high purity argon is adequate for some experiments, we have installed a secondary purification system consisting of passage over Ti/Zr sponge at high temperature followed by passage through a molecular sieve. Our experiments have shown that we are able to measure NCl(a) time decays with exponential time constants considerably longer than 100 ms. A typical time decay is shown in Figure 7.

Figure 8 shows preliminary data taken for a variety of ClN_3 densities, as a plot of exponential decay rate vs. the ClN_3 density. Clearly, the scatter is large and the intercept at $[ClN_3] = 0$, corresponding to the radiative rate, is very uncertain. The scatter in the data points stems in large measure from the uncertainty in the azide density. The percentage of the azide in the flow, measured upstream of the cell, appears to have considerable error for small flows. This is understandable in terms of a finite amount of the azide being lost on the walls of the transport tubes and the cell. This also leads to a problem in establishing the true zero of the ClN_3 flow rate; some azide is coming off the walls of the system even when there is no readable flow from the generator. We hope to remedy this situation by using static fills of the cell and in-situ determinations of the azide density. Also, greater laser fluences would be desirable, because the signal to noise ratios would be greater at the low azide flows. We hope that these modifications will allow us to determine the NCl a $-->$ X radiative rate in the near future.
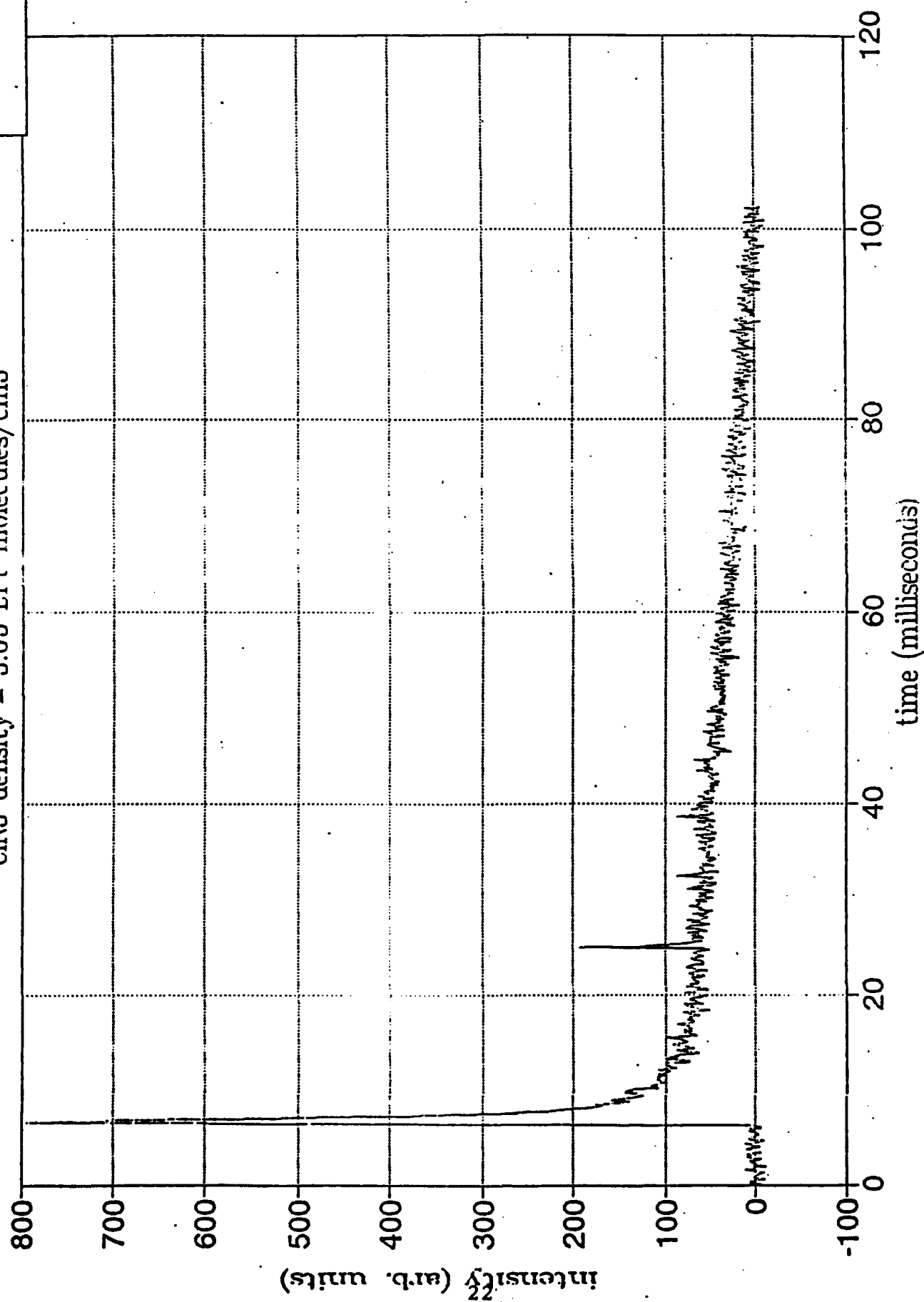
Figure 7. Typical NCl a --> time decay

Density of ClN3 vs Rate of NCl(a) decay
02.21 and 02.28.92, at 4.5 Torr

y-intercept=23.4+2.0 1/s

decay rate (1/s)

ClN3 density (°E12 molecules/cm3)
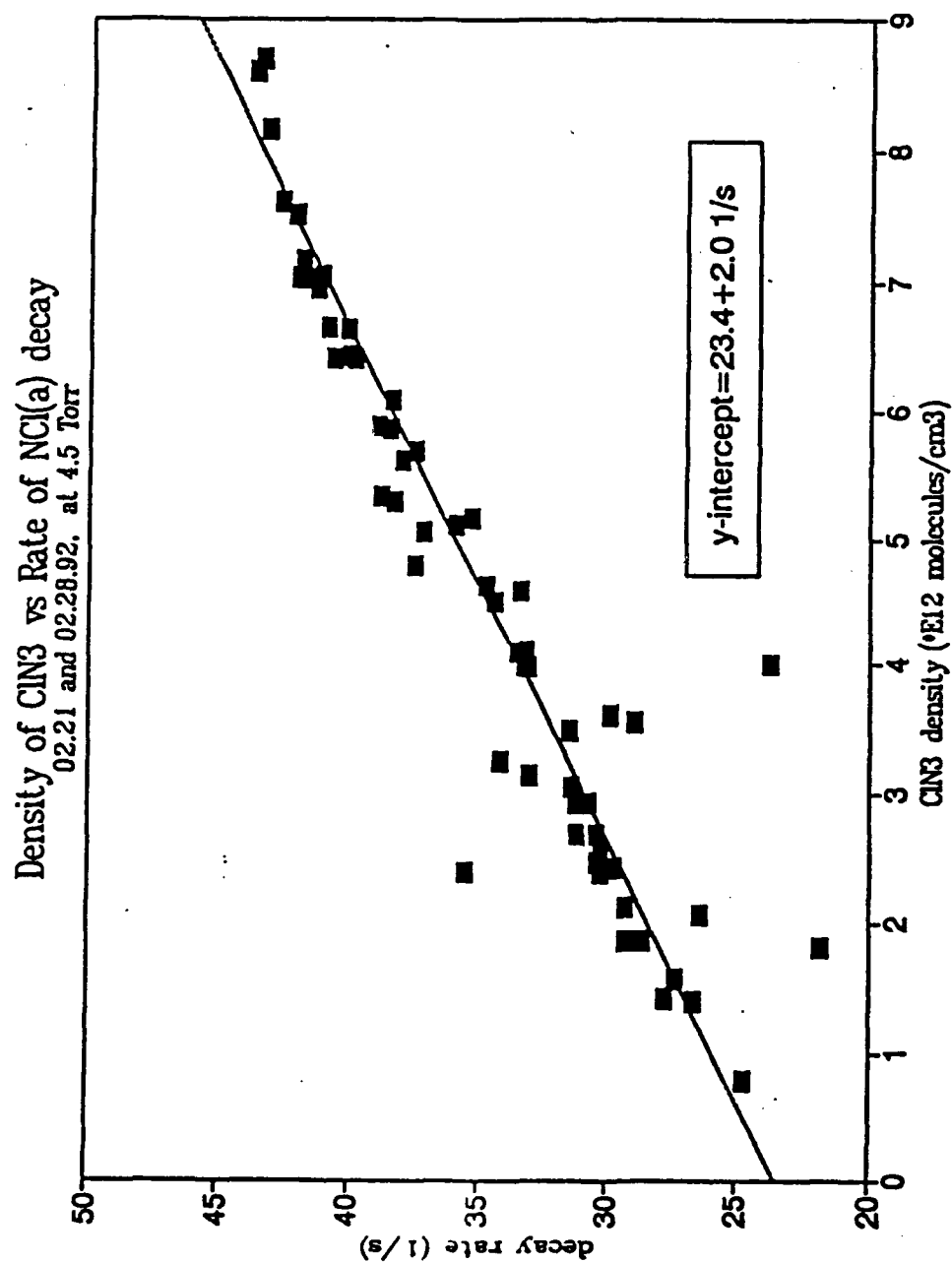
Figure 8. Plot of the rate of decay of NCl a --> X emission vs. the ClN_3 density.

Even in its present configuration, the experiment should allow the determination of the NBr a --> X rate, which is expected to be considerably greater than that for NCl.

Clearly, these experiments also afford us the opportunity to measure rate constants for quenching of NCl(a) by collisions with various added species. Although rate constants for quenching of $O_2(a^1\Delta)$ and $NF(a^1\Delta)$ by many species are known, virtually no similar data exists for $NCl(a^1\Delta)$, with the exception of the NCl(a)/I rate noted above. During this reporting period, we began a study of these collisional quenching rates by investigating the quenching of NCl(a) by O_2. This process is particularly interesting since a near resonant energy exchange is possible as follows:

$$NCl(a,v=0) + O_2(X,v=0) \xrightleftharpoons{} NCl(X,v=0) + O_2(a,v=1) \qquad (10)$$

This process is endothermic by only 60 cm^{-1}, such that at high NCl(a) and O_2 densities an equilibrium might well be established. If so, this process might be very significant with respect to chemical pumping of iodine lasers, since it is now well established that both NCl(a) and $O_2(a)$ can efficiently pump I^*. In this sense, chemical ···· for generation of NCl(a), such as those described above, ··· offer an alternative to the conventional[18] wet chemistry ···· ds for generating $O_2(a)$.

Since only small densities of NCl(a) are generated in our pulsed photolysis experiments relative to the amounts of add O_2, it was expected that we would observe simple quenching of the NCl(a) by O_2, such that we might measure the rate of this pro-

the rate constant for this process is near 5×10^{-12} $cm^3 s^{-1}$, and our initial objective was simply to verify this result. The experiments involved 193 nm photolysis of ClN_3 diluted heavily in argon, as above, in the presence of various densities of O_2. Figure 9 shows the unexpected results which were obtained. The O_2 served to reduce the intensity of the NCl a $-->$ X emission, but did not change the time constant of the decay. The intensity reduction appeared to be in proportion to the amount of O_2 present; an O_2 pressure of 50 mTorr was sufficient to almost completely attenuate the emission. Since the O_2 is in large excess over the initial amount of NCl(a) made by the photolysis, this result cannot be attributable to an equilibration according to Eqn. (10) above. Nonetheless, there must be some process operating which regenerates the NCl(a) after it is quenched by the O_2. A likely candidate for this process is

$$O_2(a^1\Delta) + ClN_3 --> O_2(X) + NCl(a^1\Delta) + N_2 \qquad (11)$$
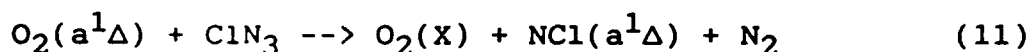
This process is completely analogous to the thermal dissociation of ClN_3, which has been shown[5] to generate NCl(a). The energy carried by O_2(a) is easily sufficient to break the weak N-N bond in ground state ClN_3, which correlates adiabatically with NCl(a) + N_2. We are continuing to investigate this process and others like it, as they offer a means to extract the energy stored in the azide in a manner which can be useful for high energy lasers.

Figure 9. Time profile of NCl a --> X emission in the presence of various densities of O_2.
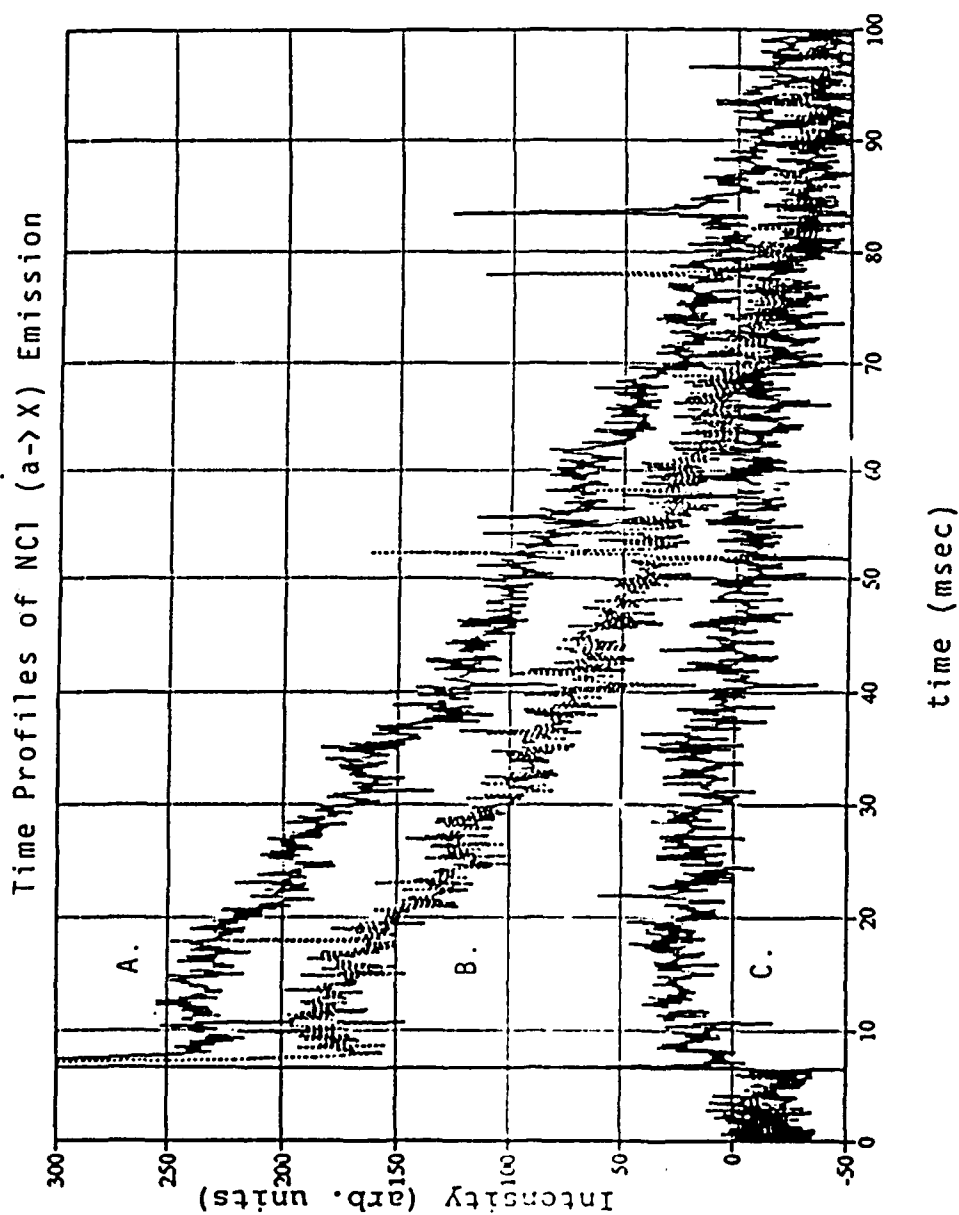
ClN_3 density - 1.5×10^{11} cm^{-3}

A. no O_2
B. 22 μ O_2 (7.1×10^{14} cm^{-3})
C. 40 μ O_2 (1.3×10^{15} cm^{-3})

PUBLICATIONS FROM THIS WORK

D. B. Exton, J. V. Gilbert, and R. D. Coombe, "Kinetics and Mechanism of the Reaction of $NFCl_2$ with Excess Hydrogen Atoms," J. Phys. Chem., 95, 7758 (1992).

R. W. Schwenz, J. V. Gilbert, and R. D. Coombe, "Initial Scale-Up of the Reaction of NCl_3 with Hydrogen Atoms: Chemical Pumping of Excited $I(^2P_{1/2})$," manuscript in preparation for submission to Chem. Phys. Lett.

PRESENTATIONS

A. J. Navritil and R. D. Coombe, "Energy Transfer from $NCl(a^1\Delta)$ to Iodine Atoms," presented at the XXth Informal Conference on Phorochemistry, Atlanta, April 1992.

R. W. Schwenz and R. D. Coombe, "Initial Scale-Up of the Reaction of NCl_3 with Hydrogen Atoms," presented at the XXth Informal Conference on Photochemistry, Atlanta, April 1992.

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